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RESEARCH ARTICLE

SYNTHESIS AND CHARACTERIZATION OF AN Al^{3+}-SELECTIVE FLUORESCENT PROBE DERIVED FROM BENZOYL HYDRAZINE

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ABSTRACT

Al^{3+} plays important roles in biological and environmental process, so the detection of Al^{3+} attracts the intrest of many scientists. Among the detection methods, fluorescent probe method has many advantages such as high sensitivity and good selectivity, and has become an important detection method for the analysis of Al^{3+} in vivo/vitro. In this work, a fluorescent probe **P** derived from benzoyl hydrazine was synthesized and characterized as an Al^{3+}-selective probe. Compared to other tested metal ions, P shows better selectivity to Al^{3+} in ethnol solution, a linear relationship was found between the fluorescence intensity at 444 nm from 5.0×10^{-6} to 2.0×10^{-5} M of Al^{3+} concentration with a detection limit of 1.7×10^{-6} M of Al^{3+}. Job's plot revealed that **P** and Al^{3+} formed a complex in 1:1 stoichiometry.

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INTRODUCTION

The development of increasingly selective and sensitive methods for the determination of biologically and environmentally relative targets is currently receiving considerable attention.[1-3] Among the various detection methods available, fluorescence method still remains the most frequently used mode for the recognition of important analytes due to its high selectivity and easy operational use.[4-7] Al^{3+} plays important roles in biological and environmental processes, so the development of Al^{3+} sensing materials with high selectivity and sensitivity is attracting increasing attention in analytical, biological and environmental sciences. Fluorescent probes derived from benzoyl hydrazine were easy to prepare and have been used widely for the detection of metal ions. Based on our previous work,[8-10] a new fluorescent probe **P** derived from benzoyl hydrazine was synthesized and characterized as an "off-on" type of Al^{3+}-selective probe (Scheme 1).

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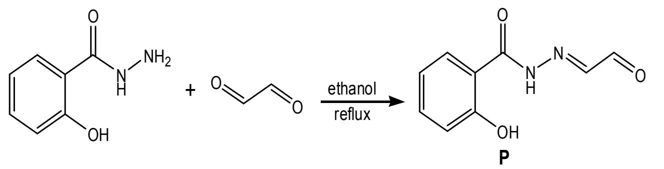


Scheme 1 Synthesis route of probe P.

Experimental Section

Reagents and Instruments: All reagents are commercially available and used directly. Fluorescence spectra were obtained on a Hitachi F-4600 spectrophotometric. Mass spectra were recorded on a Thermo TSQ Quantum Access Agillent 1100 system. Nuclear magnetic resonance spectra were measured with a Bruker AV 400 instrument and chemical shifts are given in ppm from tetramethylsilane (TMS).

Synthesis of Probe P: The solution of 2-hydroxy benzoyl hydrazine 0.5 g (3.3 mmol) and glyoxal 5 mL (25.8 mmol) in ethanol (60 mL) was stirred and refluxed under N_2 atmosphere for 4 h, and then the solution was cooled to room temperature, the yellow precipitate so obtained was filtered off and dried in vacuum and used directly. MS (EI) m/z: 190.8 $[M-H^+]^-$. ^1H NMR (400 MHz, DMSO), δ (ppm): 12.00 (s, 1H), 11.51 (s, 1H), 8.18 (s, 1H), 7.81 (d, 1H, J=8.04), 7.45 (t, 1H, J=7.40), 6.98 (d, 1H, J=8.32), 6.95 (d, 1H, J=7.44).

General Spectroscopic Methods: Metal ions and probe **P** were dissolved in deionized water and DMSO to obtain 1.0 mM stock solutions, respectively. Before spectroscopic measurements, the solution was freshly prepared by diluting the high concentration stock solution to the corresponding desired concentration. For all measurements, excitation and emission slit widths were 10/10 nm, excitation wavelength was 350 nm. Fluorescent studies were carried out in ethanol.

RESULTS AND DISCUSSION

Selectivity study of P: Selectivity of **P** was firstly studied and the results was shown in **Figure 1**, the testing ions are Na^+, K^+, Al^{3+}, Ag^+, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe^{2+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+} and Fe^{3+}. From the results, only the addition of Al^{3+} caused the enhancement of fluoresence of **P** at the wavelength of 444 nm in ethonal, so the proposed **P** has better selectivity to Al^{3+} than to other tested metal ions.

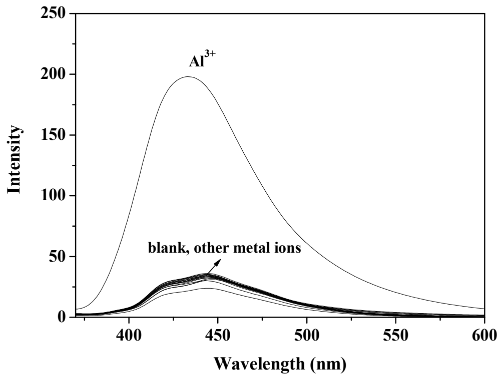


Figure 1. Selectivity of P (10 μM) to different metal ions (100 μM) in ethanol

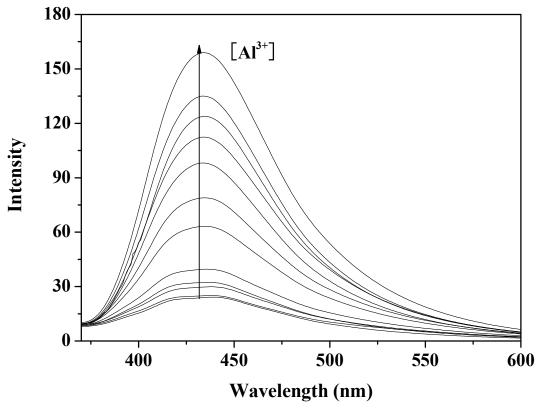


Figure 2. Fluorescence response of P (10 μM) to various concentrations of Al^{3+} in ethanol

Fluorescent titration of P: As shown in **Figure 2**, the fluorescence titration of Al^{3+} was performed using a 10 μM solution of **P** in ethanol. With the addition of Al^{3+}, a gradual increase in the fluorescence intensity of **P** at 444 nm, and the linear range of **P** to Al^{3+} was from 5.0×10^{-6} to 2.0×10^{-5} M with a detection limit of 1.7×10^{-6} M of Al^{3+}.

Sensing mechanism of P with Al^{3+}: In order to study the coordination mode of **P** with Al^{3+}, job's plot experiment was carried out and the analysis showed a 1:1 stoichiometry for the **P**–Al^{3+} complex (**Figure 3**). According to the results, possible sensing mechanism of **P** with Al^{3+} was showed in **Scheme 2**.

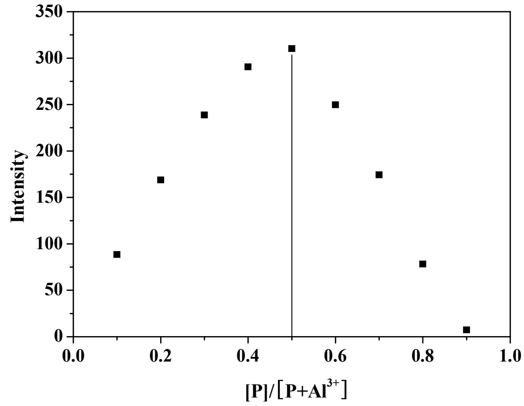
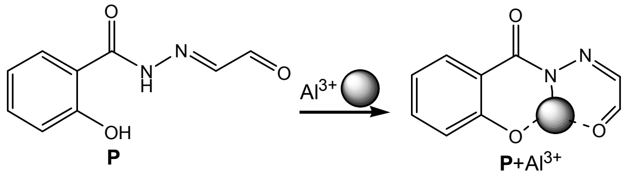


Figure 3. Job's plot of P with Al^{3+}. Total concentration of Al^{3+} and P was kept at fixed 50 μM.



Scheme 2. Proposed binding mode of P with Al^{3+}.

Reversibility of P to Al^{3+} : It is believed that this process is not reversible, which has been proved by the test using EDTA-Al^{3+} as seen in Figure 4. Without Al^{3+}, P existed in a unconstrained C=N form (Figure 4a), addition of Al^{3+} led to the coordination with the ligand groups, resulting in a constrained C=N form along with an obvious fluorescence enhancement at 444 nm (Figure 4b). The addition of 5 folds of EDTA decreased the fluorescence intensity, and add another more 10 folds of Al^{3+}, the fluorescence intensity increased again. It is very likely due to the chelaton–induced constrained C=N form. Thus, an "off-on" based probe for Al^{3+} was constructed.

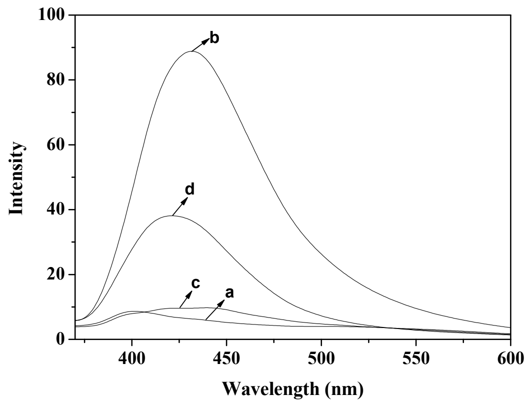


Figure 4 Reversible experiment of P with Al^{3+} in ethanol. a. P (10μM), b. P (10 μM) + Al^{3+} (10 μM), c. P (10 μM) + Al^{3+} (10 μM) + EDTA (50 μM), d. P (10 μM) + Al^{3+} (10 μM) + EDTA (50 μM) + Al^{3+} (100 μM)

Conclusion

A benzoyl hydrazine derivative was synthesized and characterized as Al^{3+}-selective fluorescent probe.

This probe has good selectivity and sensitivity to Al^{3+} in ethanol compared to other tested metal ions.

Acknowledgments

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